

Measurement of the Diffusion Coefficient of Miscible Fluids using both Interferometry and Wiener's Method¹

N. Rashidnia² , R. Balasubramaniam², J. Kuang³ , P. Petitjeans^{3,4} and T. Maxworthy^{3,4}

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²National Center for Microgravity Research on Fluids and Combustion, NASA Glenn Research Center, Cleveland, Ohio.

³Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, California.

⁴PMMH-ESPCI, 10, Rue Vauquelin, Paris, 90075, France.

Abstract

We report measurements of the diffusion coefficient of two miscible liquids. The liquids are various combinations of pure silicone oils and those to which small amounts of solvents are added to control the difference in density between the fluids. The liquids were placed in a quartz cell such that the interface is initially horizontal. As the fluids diffuse, the profile of the index of refraction near the interface is time dependent, and is related to the local concentration of the diffusing fluids. The concentration gradient profile has been measured by a shearing interferometer incorporating a Wollaston prism, as well as Wiener's method. In the latter technique, a 45° light sheet is passed through the test cell, and the local deflection of the light beam has been measured. The average diffusion coefficient was obtained by analysis of the measured concentration gradient profile, assuming that the diffusion process is one-dimensional and is characterized by a constant value of the diffusion coefficient.

KEY WORDS: Diffusion coefficient; interferometry; miscible interfaces; Wiener's method.

1 Introduction

The dynamics of miscible interfaces is an active area of research that has been identified to benefit from experimentation in reduced gravity. The goal is to study the patterns assumed by the interface when one liquid is slowly displaced by another in a cylindrical tube, such that diffusion plays an important role in the dynamics. It has been suggested that non-traditional stresses in the fluids, caused by the steep variation of the concentration of the miscible fluids in the mixing zone, might be important in the dynamics [1]. These effects are overwhelmed by the flow caused by buoyancy under terrestrial conditions [2]. An improved understanding of the dynamics of multiphase porous media flows is deemed essential for progress in the fields of enhanced oil recovery, fixed bed regeneration, hydrology and filtration [3, 4, 5].

The diffusion coefficient of the miscible fluids is a property that is important in the dynamics. Its values are vitally important to the proper design of the reduced gravity experiments. In particular, it determines the desirable range for the speeds of the displacing fluids, so that the effect of diffusion is not overshadowed by convective transport of mass. Petitjeans and Maxworthy [3] used a variation of Wiener's Method, described in [6], to measure the diffusion coefficient. A focused laser beam was passed through a quartz cell in which two liquids were diffusing into each other across a horizontal miscible interface. The index of refraction at any location in the test cell is a function of time and depends on the local concentration of the fluids. As the beam traversed the test cell, it was bent vertically when it traversed a vertical gradient of concentration, and the deflection of the exiting beam was measured as a function of vertical position using a light detector. The deflection angle is related to the

vertical gradient of the index of refraction, and hence to the concentration gradient within the test cell. The average diffusion coefficient was obtained by analysis of the measured concentration gradient profile, assuming that the diffusion process is one-dimensional and is characterized by a constant value of the diffusion coefficient. The method used by Petitjeans and Maxworthy to measure the concentration gradient is a point measurement that requires the light beam and the detector to be traversed through the region of interest. Therefore instantaneous measurement of the concentration gradient cannot be obtained everywhere near the interface. To overcome this limitation, we have used both interferometry and the original Wiener Method, that used a 45° light sheet, to obtain the distribution of the index of refraction in the mixing region. Specifically, in the first technique we have used a shearing interferometer incorporating a Wollaston prism, operating in the finite fringe mode, to visualize the concentration gradient in the mixing zone. The diffusion coefficient is obtained from the measured concentration gradient profiles following the procedure used by Petitjeans and Maxworthy. In what follows, we describe the measurement techniques and the measured diffusion coefficients for various combinations of pure silicone oils and those to which small amounts of decane or carbon tetrachloride are added to control the mixture density.

2 Measurement techniques

2.1 Shearing interferometry using a Wollaston prism

A shearing interferometer measures the gradient of the index of refraction in a certain direction within a test cell [7]. We have used a Wollaston prism to shear the light beam. A

collimated, polarized beam of light from a laser is passed through a transparent test cell. The light is then focused on a Wollaston prism, which splits the light into two beams that are slightly displaced from each other. When the beams are recombined, they produce interference fringes that indicates gradients in the index of refraction in the test medium. We have used the interferometer in what is called the finite fringe mode where equidistant, parallel interference fringes appear in a uniform index of refraction field in the test cell. This is the case when only one of the fluids is present in the test cell. When the second fluid is introduced and diffusion occurs, the deviation or shift of a fringe from its undisturbed location is a measure of the index of refraction gradient within the test cell. We assume that the index of refraction within the test cell is only a function of the vertical coordinate. The light beam is passed through the test cell horizontally, and we assume that each ray of light traverses a path of constant refractive index, without refraction. Figure 1 shows a schematic of the Wollaston prism shearing interferometer. The inset at the top of the figure shows the fringe shift that results from the diffusion across a decane - 50 *cs* silicone oil interface, contained in a quartz test cell of 10×10 *mm* cross-ecction, at approximately thirty minutes after the fluids were brought into contact. This fringe represents the instantaneous profile of the gradient of the index of refraction near the interface of the diffusing fluids. To obtain this image, the Wollaston prism was rotated such that the interfering beams are nearly horizontally separated.

2.2 Wiener's method

A schematic of the experimental setup for Wiener's method is shown in Figure 2. A test cell containing the diffusing fluids is illuminated by a laser light sheet, at a 45° angle to the

interface. As the light traverses the test cell, the exiting rays are bent vertically when they cross a vertical gradient of concentration. The angle of deflection of the light exiting the test cell is given by

$$\alpha = \frac{n}{n_a} \int \frac{1}{n} \frac{\partial n}{\partial x} dz \quad (1)$$

where n (with respect to the value n_a for air) is the refractive index of the fluid, x is perpendicular to the mixing front, and z is the direction of propagation of the undisturbed laser light. Figure 2(c) shows a typical image of the light exiting the test cell. The concentration gradient at a given x_{in} along the light sheet is proportional to the deflection $x_{out} - x_{in}$ of the exiting light. The plot of $x_{out} - x_{in}$ versus x_{in} therefore represents the profile of the concentration gradient in the test cell.

2.3 Diffusion coefficient calculation

We assume that the two fluids are pure, and therefore only binary diffusion occurs. Let $\rho_1(x, t)$ and $\rho_2(x, t)$ represent the mass concentration (mass of species per unit volume of the fluid) of the two fluids at a vertical location x and a given time t . Far away from the interface, $\rho_{1\infty}$ and $\rho_{2\infty}$ are the density of the two fluids. It is convenient to define $c = \frac{\rho_1(x)}{M_1 \rho_{1\infty}}$ as the dimensionless molar concentration of fluid 1, where M_1 is the molecular weight of fluid 1. A similar dimensionless concentration for fluid 2 may be defined. For stationary liquids, the governing equation for diffusion is [8]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

Strictly speaking, this equation is valid only when the binary diffusion coefficient D as well

as the local density in the fluid is constant. We will extract the diffusion coefficient from our experiments assuming that the above equation is valid. The boundary conditions are

$$c \rightarrow 1 \text{ as } x \rightarrow \infty \quad \text{and} \quad c \rightarrow 0 \text{ as } x \rightarrow -\infty \quad (3)$$

The solution for the concentration gradient is

$$\frac{\partial c}{\partial x} = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \quad (4)$$

The dimensionless concentration gradient profile for fluid 2 is identical to that for fluid 1. Assuming that the refractive index is linearly proportional to the concentration of the two fluids, the gradient of the refractive index has a similar profile.

The maximum value of the concentration gradient is at $x = 0$ and is given by

$$m = \left(\frac{\partial c}{\partial x} \right)_{max} = \frac{1}{2\sqrt{\pi Dt}} \quad (5)$$

For positive x , let $x = \frac{1}{2}\delta_{1-\frac{1}{e}}$ at the location where $\frac{\partial c}{\partial x} = \left(1 - \frac{1}{e}\right) m$. Using the solution given above, we can then obtain the diffusion coefficient to be

$$D_{1-\frac{1}{e}} = \frac{\delta_{1-\frac{1}{e}}^2}{\left[-16 \ln \left(1 - \frac{1}{e}\right)\right] t} = \frac{\delta_{1-\frac{1}{e}}^2}{7.334t} \quad (6)$$

Similarly, let $x = \frac{1}{2}\delta_{\frac{1}{e}}$ at the location where $\frac{\partial c}{\partial x} = \frac{1}{e}m$. $D_{\frac{1}{e}}$ is then obtained to be

$$D_{\frac{1}{e}} = \frac{\delta_{\frac{1}{e}}^2}{16t} \quad (7)$$

Wiener [6] obtained the diffusion coefficient by measuring the maximum deflection γ of the light beam that exits the test cell. From the solution given above, it can be shown that

$\gamma = \frac{|n_1 - n_2|d}{2\sqrt{\pi Dt}}$, where d is the width of the test cell. The diffusion coefficient is given by

$$D_{Wiener} = \frac{(n_1 - n_2)^2 d^2}{4\pi \gamma^2 t} \quad (8)$$

The values of $\delta_{1-\frac{1}{e}}$, $\delta_{\frac{1}{e}}$ and γ have been obtained from the measured refractive index gradient profiles, for various values of t . A plot of δ^2 versus t was then generated (a typical plot is shown in Figure 3). Values for the diffusion coefficient, together with its 95% confidence interval, were obtained by finding the best fitting straight line to such plots, using linear regression.

3 Results

Table 1 shows the measured diffusion coefficients for several liquid pairs, chiefly silicone oils. These fluids are currently planned to be used in the reduced gravity experiments described in [2], and the diffusion coefficients are unknown, to the best of our knowledge. In some instances, small quantities of solvents such as decane or carbon tetrachloride were added to one of the fluids so that the density of the two fluids were the same. We have obtained a diffusion coefficient for such cases assume that the simple theory of binary diffusion holds. In all cases, we have reported the 95% confidence interval for the measured diffusion coefficients, obtained from the regression analysis. The diffusion coefficient measured by Wiener's original method appears to be the least accurate, perhaps because the refractive index of the fluids must be known more precisely at the wavelength of the light used. In the case of diffusion across a 1000 *cs* / 1 *cs* interface, the difference in the diffusion coefficients obtained by the various techniques is large. This pair has the largest density difference ($\frac{\Delta\rho}{\rho} = 0.19$) among all the fluid pairs we have used. It is possible that the simple model of diffusion we have used does not hold for this pair.

References

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Table 1. Measured diffusion coefficients

Fluids	Diffusion coefficient (cm^2/s)			
	$D_{1-\frac{1}{e}}$	$D_{\frac{1}{e}}$	D_{Wiener}	Technique
1000 <i>cs</i> / 100 <i>cs</i>	$(4.36 \pm 0.30) \times 10^{-8}$	$(4.79 \pm 0.22) \times 10^{-8}$	$(1.69 \pm 0.06) \times 10^{-8}$	WM
silicone oils	$(5.11 \pm 0.73) \times 10^{-8}$	$(5.41 \pm 0.75) \times 10^{-8}$	-	WPI
1000 <i>cs</i> / 50 <i>cs</i>	$(4.37 \pm 0.97) \times 10^{-8}$	$(5.07 \pm 1.31) \times 10^{-8}$	-	WPI
1000 <i>cs</i> / 10 <i>cs</i>	$(2.61 \pm 0.10) \times 10^{-7}$	$(2.47 \pm 0.10) \times 10^{-7}$	$(3.14 \pm 0.15) \times 10^{-7}$	WM
silicone oils	$(2.83 \pm 0.72) \times 10^{-7}$	$(2.34 \pm 0.68) \times 10^{-7}$	-	WPI
1000 <i>cs</i> / 1 <i>cs</i>	$(4.17 \pm 0.23) \times 10^{-6}$	$(2.48 \pm 0.21) \times 10^{-6}$	$(1.93 \pm 0.08) \times 10^{-6}$	WM
silicone oils	$(2.65 \pm 0.32) \times 10^{-6}$	$(1.93 \pm 0.29) \times 10^{-6}$	-	WPI
1000 <i>cs</i> silicone oil + decane* / 10 <i>cs</i> silicone oil	$(3.28 \pm 0.12) \times 10^{-7}$	$(3.09 \pm 0.13) \times 10^{-7}$	-	WM
1000 <i>cs</i> silicone oil / CCl_4 +100 <i>cs</i> silicone oil**	$(2.71 \pm 0.43) \times 10^{-8}$	$(3.02 \pm 0.36) \times 10^{-8}$	-	WM
100 <i>cs</i> silicone oil/ decane	$(2.82 \pm 0.09) \times 10^{-6}$	$(3.02 \pm 0.12) \times 10^{-6}$	-	WM
50 <i>cs</i> silicone oil / decane	$(1.54 \pm 0.40) \times 10^{-6}$	$(2.63 \pm 0.68) \times 10^{-6}$	-	WPI

WM - Wiener's method

WPI - Wollaston prism interferometry

* mixture density = 0.964 g/ml

** mixture density = 0.97 g/ml

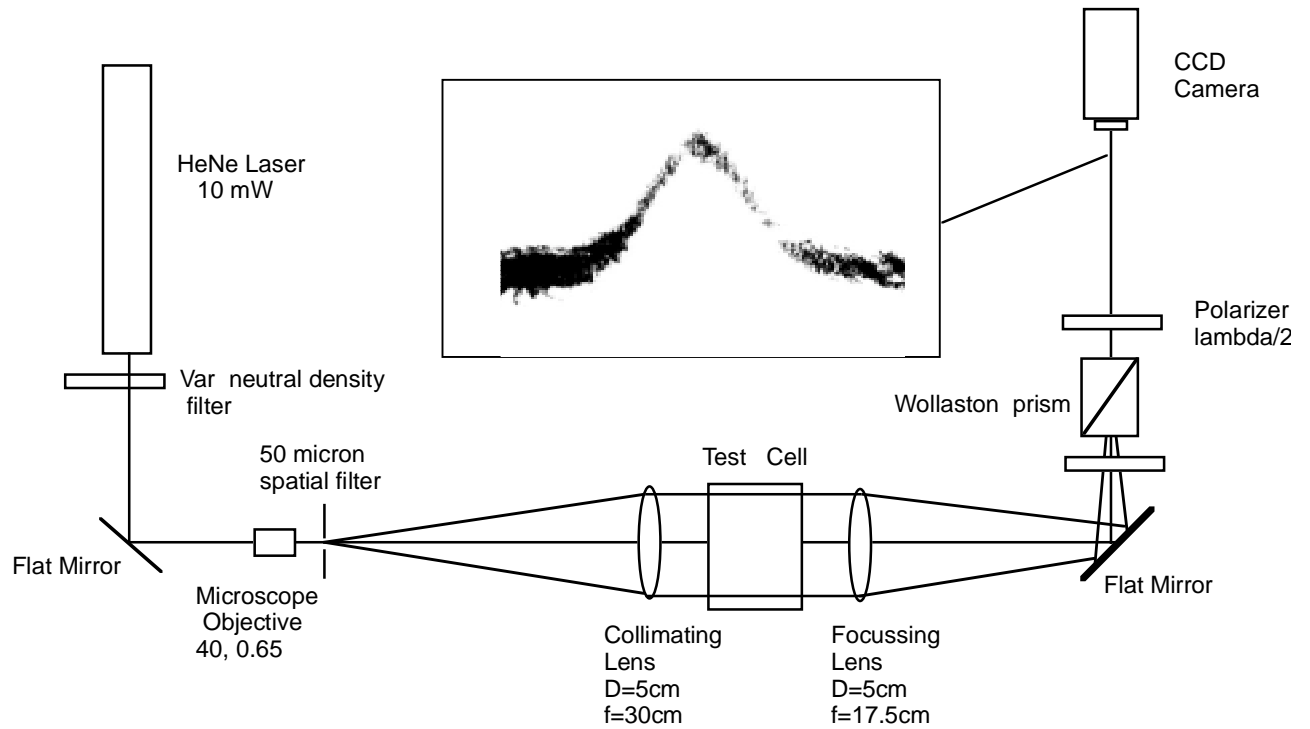
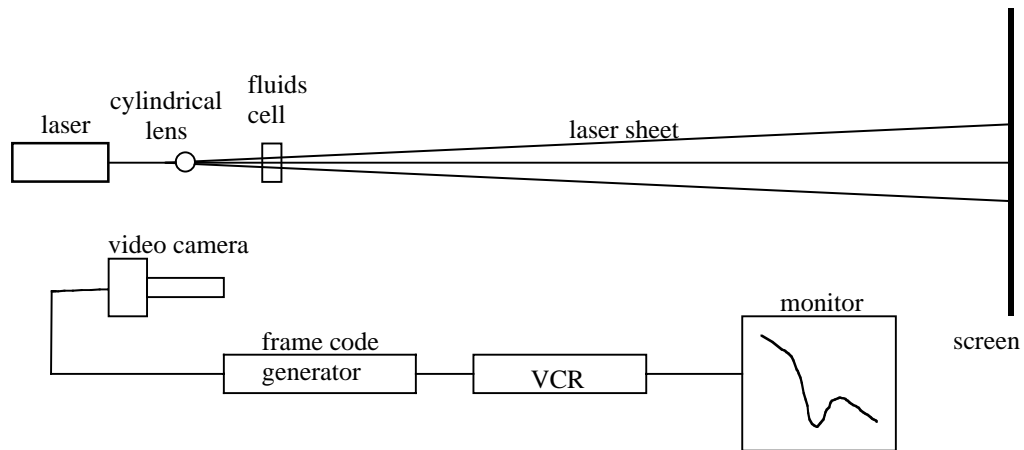
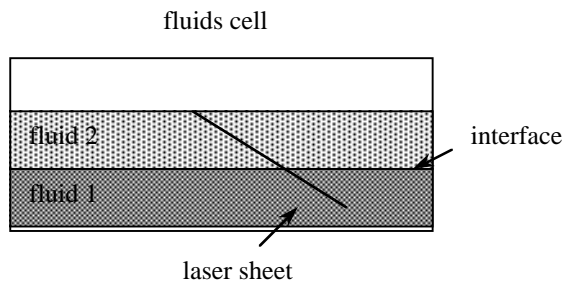


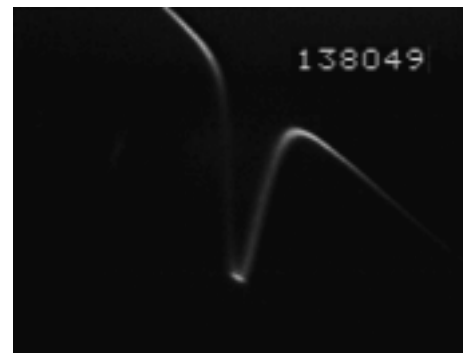
Figure 1. A schematic of a Wollaston prism shearing interferometer. Shown in the inset is the fringe shift caused by diffusion across a decane - 50 *cs* silicone oil miscible interface.



(a)



(b)



(c)

Figure 2. A schematic of Wiener's method (a) experimental setup (b) test cell and light sheet location (c) image showing the deflection of the light sheet.

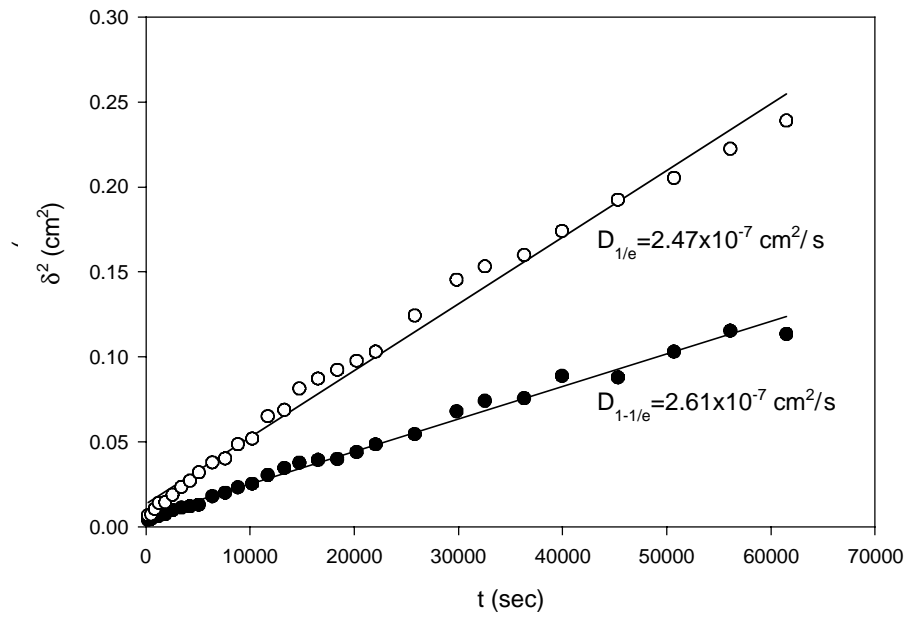


Figure 3. A plot of δ^2 (see Section 2.3) versus time, for the diffusion of a 10 *cs* - 1000 *cs* silicone oil fluid pair. The diffusion coefficient is obtained from the slope of the best fitting line.